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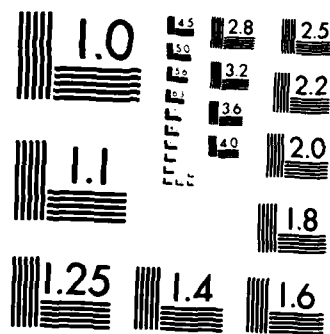UNCLASSIFIED   AFOSR-TR-84-1208 F49620-81-C-0030   F/G 21/2   NL

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IONIC MECHANISMS OF SOOT FORMATION IN FLAMES

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May 1984

Final Report for Period 1 April 1981 to 31 July 1983

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Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
BOLLING AIR FORCE BASE
WASHINGTON, DC 20332

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FOREWORD AND ACKNOWLEDGMENTS

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
	Approved for public release; distribution unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
TP-443	AFOSR-TR- 84-1208

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
AeroChem Research Laboratories Inc.		AFOSR/NA

6c. ADDRESS (City, State and ZIP Code)	7b. ADDRESS (City, State and ZIP Code)
P.O. Box 12 Princeton, NJ 08542	Bolling AFB DC 20332-6448

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Air Force Office of Scientific Research	NA	F49620-81-C-0030

8c. ADDRESS (City, State and ZIP Code)	10. SOURCE OF FUNDING NOS.			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
BOLLING AFB DC 20332				

11. TITLE (Include Security Classification) Ionic Mechanisms of Soot Formation in Flames	61102F	2308	A2	

12. PERSONAL AUTHOR(S)
Calcote, Hartwell F. and Olson, Douglas B.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Final	FROM 81/4/1 TO 83/7/31	1984, May	30

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB GR.	Soot Formation, Smoke, Ions in Flames, Ion-molecule Reactions, Flames, Combustion

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The chemi-ion, ion-molecule mechanism of soot nucleation has been further examined by studies in premixed flames with Langmuir probes, molecular beam ion sampling mass spectrometry, and by flame temperature measurements. Langmuir probes were used to obtain absolute total ion concentrations in acetylene-oxygen flames over a range of equivalence ratios extending from stoichiometric mixtures to very sooty flames. These data were used in a preliminary calibration of the mass spectrometer. Two peaks in both total and individual positive ion concentration profiles were identified preceding the appearance of soot--the second peak occurred only at equivalence ratios very near the soot point or in sooty flames. The peak ion concentration decreased with increasing equivalence ratio well beyond the threshold equivalence ratio for soot formation. This refutes one of the arguments that has been used against the proposed mechanism, namely that ion concentrations increase at the equivalence ratio for soot formation. Means of treating particle electronics involved in sooty flames have been organized and applied to explain the

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS ☐	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
JULIAN M TISHKOFF	(202) 767-4935	NA

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(block 19, continued)

effect of chemical additives on soot production. The effect of flame temperature (1700 to 2400 K) on soot threshold and soot yield was determined for a series of fuels. Increasing flame temperatures increased the soot threshold equivalence ratio with a small temperature dependence, and decreased the soot volume fraction with a large temperature dependence.

The results continue to support the chemi-ion, ion-molecule mechanism of soot nucleation.

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I. INTRODUCTION AND STATEMENT OF WORK

The mechanism of smoke, i.e., soot, formation in flames remains one of the major unsolved problems in combustion research, even though it has been the subject of study for decades. The problem persists because soot formation involves a chemical system with dozens of reacting species and hundreds of reactions and equilibria, and it involves a phase change from a purely gaseous system to a gas-particle system. Nonetheless, progress is being made. The detailed chemical kinetics of numerous combustion systems relevant to soot formation have been established[1]; the surface growth process on soot,[2] and the agglomeration of soot particles[3] are fairly well understood. There is disagreement as to the relative importance of soot nucleation on the quantity of soot produced in sooting flames. Harris[2] argues that the final amount of soot formed in a given system is mainly determined by the particle nucleation process; that is, flames which produce a larger total quantity of soot do so because they produce more particles rather than because the soot particles are larger. On the other hand coagulation theory, confirmed by at least some experiments,[4] indicates that the final number density of particles is independent of the nucleation process. Prado et al.,[4] however, agree that the first appearance of soot is controlled by the nucleation process. Thus the initial transition from a fuel-rich flame to a soot-containing flame appears to be the most important (in a practical sense) as well as the least understood step in this process. We refer to this transition as "nucleation" of soot particles, even though the process is quite different from homogeneous nucleation of a supersaturated vapor.

There is no agreement as to whether the mechanism of initial soot formation primarily involves charged ionic species or neutral molecules and free radicals. AeroChem has championed[5-9] the hypothesis that soot nucleation is governed by a series of rapid ion-molecule reactions building upon the chemi-ion $C_3H_3^+$. This is not a new concept; it had been suggested by several previous workers[10-14] but had never been explored in any great detail. Progress in confirming this hypothesis in the present program has been significant. There are still, however, a number of questions to be answered before it will be perfectly clear that soot is formed through an ionic nucleation mechanism.

The significance of smoke formation to the Air Force mission is well-established. Primarily, soot produced in the combustor of a turbojet engine greatly increases the radiative heat transfer to the metal combustor walls, raising their temperature, and thereby significantly reducing the service lifetimes

of these combustor liners.[15] Aircraft engine overhauls are expensive, and, in general, the current generation of engines has lifetimes of about half that of the previous generation. This is partially due to the higher pressure ratios used in current engines but also due to the use of fuels which, although within current military specifications, contain higher fractions of hydrocarbons which produce soot (and therefore more flame radiation and higher liner temperatures). Smoke emissions from aircraft engines are also environmental and tactical problems. No pilot wants to leave a highly visible smoke trail under operational conditions.

This program was therefore directed to both a long term understanding of the basic chemistry and physics of soot formation and to more immediate evaluation of empirical relationships which would be useful to the Air Force in evaluating jet fuels with various compositions and from alternate sources and processes.

The Statement of Work from the contract reads:

1. Perform ionic species concentration measurements at high molecular weights (up to approximately 5000 amu) in premixed flames of acetylene, benzene, and hexane to provide experimental data with which to test the ionic mechanism of soot formation.

2. Calibrate the ion concentrations determined with the mass spectrometer by comparing the mass spectral data with electrostatic probe data in flames in which a single ion is dominant.

3. Perform computer simulations of rich and sooting flames to test proposed detailed mechanisms of initial soot nucleation. This study will consider three alternative reaction schemes: an ionic nucleation and growth mechanism, a butadiene intermediate neutral-radical mechanism, and a neutral-radical poly-acetylene growth mechanism.

4. Determine the effects of temperatures on soot threshold and ion concentrations in premixed flames of several representative hydrocarbon fuels. Experiments will be performed in flames with constant temperature and variable fuel-air ratio, and with constant fuel-air ratio and variable temperature by heating or cooling the unburned gases and by varying the composition of the inert diluent gas.

5. Determine quantitatively the total ion concentrations (by electrostatic probe) and the temperature at sooting threshold for a series of fuels with different tendencies to soot.

6. Interpret the above data and mechanisms in terms of the potential effects of new fuels on soot formation in air-breathing engines, and possible means of minimizing soot formation in air-breathing engines.

II. STATUS OF RESEARCH

After a brief summary of our present concept of the overall mechanism of soot formation we will summarize work done under the present contract. Some of the results of this work have been or are being published and so they will only be summarized here; other results are in various stages of completion and will be described. The publications and presentations under this contract are listed in Sections III and V.

A. THE IONIC MECHANISM OF SOOT FORMATION

Our concept of the mechanism of soot formation[5-9,16] is schematically summarized in Fig. 1. This concept involves a series of steps often referred to as "nucleation" in which a gas phase system becomes an aerosol system. It is here that AeroChem has concentrated its research efforts. The mechanism starts with the formation of a chemi-ion, e.g., $CH* + C_2H_2 = C_3H_3^+ + e^-$. Because the chemi-ion $C_3H_3^+$ is the dominant ion observed in rich hydrocarbon flames, the mechanism assumes that this species is the precursor ion. By a series of rapid ion-molecule reactions this initial ion grows in size and simultaneously loses hydrogen to form initially a single ring and then multiring aromatic molecular ions. One of the advantages of this mechanism over a free radical type mechanism is that ions are known to structurally rearrange very readily so going from a linear ion to a cyclic ion is conceivable. The species presented in Fig. 1, both ionic and neutral, have all been observed in flames. Although in each step the neutral species adding to the ion is assumed to be either acetylene or diacetylene, it is understood that other reactive species available in the flame could participate in this series of growth steps. At some point during the growth phase the ion reaches sufficient size to be indistinguishable from a particle. It should be stressed that there is no sudden demarcation between a molecular and an aerosol system. This occurs very gradually and the definition of a particle is really dependent upon the sensitivity of the measurement technique.

As the large molecular ion (or small aerosol particle) grows larger it recombines with an electron (produced in the initial chemi-ionization step) to form a neutral molecule or incipient soot particle. This particle then continues to grow by surface growth and as it becomes larger its work function for electron emission decreases, finally approaching that of bulk material. Then,
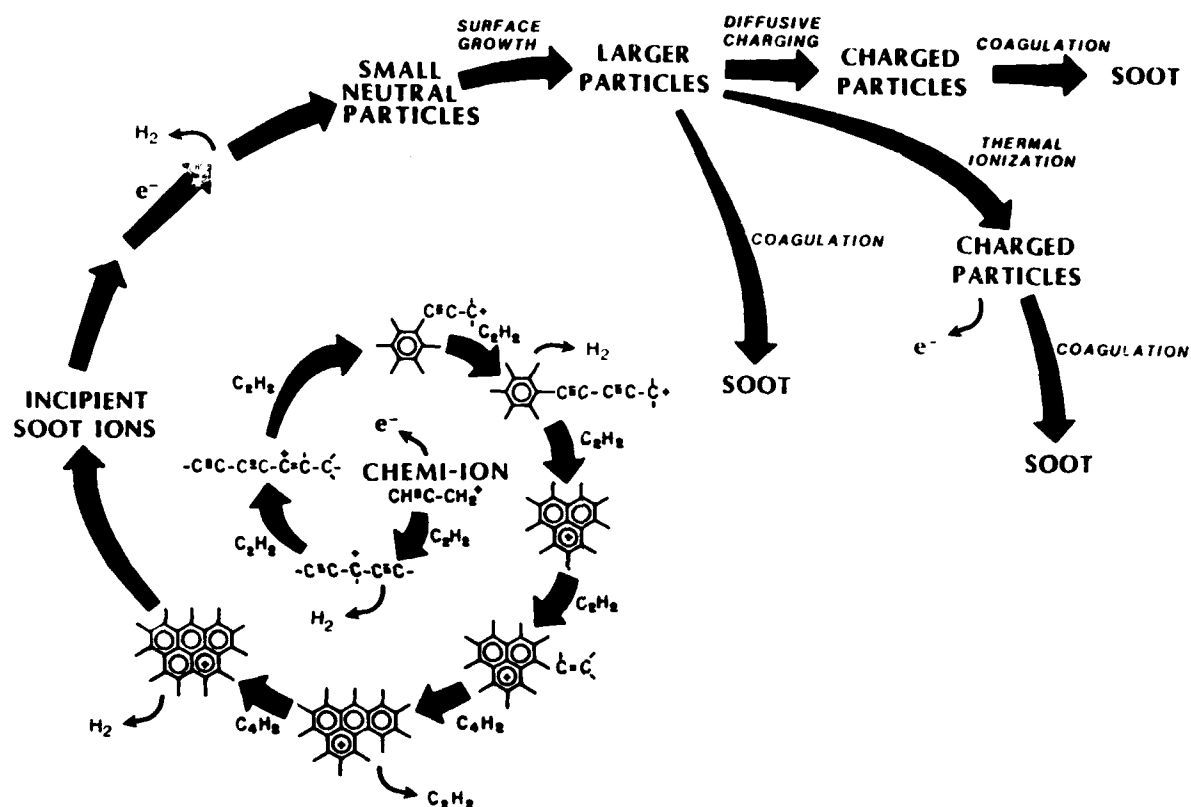
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FIGURE 1   HYPOTHESIS BEING TESTED BOTH EXPERIMENTALLY AND
THEORETICALLY

if the flame temperature is sufficiently high, the particle will thermally emit electrons and become a thermally ionized charged particle. The presence of this charge will alter its rate of coagulation with other neutral or charged particles. Thus we see that there are two stages in the growth of a soot particle in which ionic charge may be important: the nucleation step and the coagulation step. A failure to identify different processes associated with these two steps has led to considerable difficulty in the literature in terms of interpreting the role of ionized species and ionic processes.

There are also two stages in the total process represented in Fig. 1 where easily ionized chemical additives can be effective in altering the soot formation mechanism. In the nucleation stage of ion-molecule growth reactions a chemical additive may alter the ionic composition of the flame by charge transfer, e.g.,

$$C_3H_3^+ + Na = C_3H_3 + Na^+$$
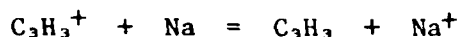
The additive might also become thermally ionized (or chemi-ionized as in the above charge transfer reaction) and alter the charge on particles by diffusive charging (P represents soot particle), e.g.,

$$P + Na^+ = PNa^+$$
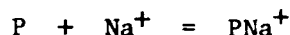
where the charge on the particle can then change the rate of coagulation.

The picture described above is in general agreement with observations on soot formation in flames but there are, however, some unexplained observations and problems and, of course, an abundance of skeptics.[17-20] The ultimate proof of this mechanism will require quantitative modeling. As the evidence continues to accumulate in support of the chemi-ionization, ion-molecule mechanism of soot nucleation, many questions remain unanswered. If we are to attain our real objective of developing a quantitative mechanism of soot formation, then it is necessary that we identify and understand all aspects of the subject. For this reason we provide here a comprehensive list of the questions relating to our proposed mechanism and to the participation of charged particles in soot formation:

1. What is the source of the double concentration peaks in both ions and neutrals which appear in flames as the equivalence ratio is increased to the point of sooting?

2. How does the rate of chemi-ion production in flames compare with the rate of soot nucleation?

3. What are the kinetics and mechanisms of $C_3H_3^+$ production in fuel-rich flames?

4. Is there any experimental or theoretical evidence that implies that molecular ions can be derived from soot particles?

5. Are the large ions observed in flames the result of sequential ion growth or the result of neutral species growth followed by equilibration with smaller ions such as $C_3H_3^+$?

6. Why do some experimental results indicate that neutral particles grow more rapidly than ionized particles?

7. Are ions important in soot formation during pyrolysis? Are chemi-ions produced in pyrolysis?

8. Can energy accumulated in a particle by exothermic growth processes lead to ionization of the particle?

9. Can chemi-ionization or thermal ionization of large molecules or large free radicals lead to the large molecular ions observed in flames?

10. What are the rates of ion-molecule reactions at flame temperatures, especially for large ions?

11. Do experiments on the electric field effects on soot formation support or disprove the chemi-ion, ion-molecule mechanism of soot nucleation?

Our long range program is directed to answering these questions.

B. PARTICLE ELECTRONICS

To support our hypothesis that the large ions observed in incipient sooting flames arise from chemi-ionization and ion-molecule reactions, and are not produced from charged particles we have reviewed the literature on particle electronics. Another motivation for this activity was to further develop the basis for quantitative modeling of soot formation. In reviewing the subject of particle electronics we formulated the quantitative expressions in a uniform manner so that they could be applied consistently, and when an appropriate expression was not available one was developed. This work is continuing; part of these results was presented as an invited paper at the First Annual Conference of The American Association for Aerosol Research in February 1982.

The processes considered are summarized below (P represents a particle, M a molecule):

<u>Thermal Ionization or Thermionic Emission</u>:

$$P \xrightarrow{\text{energy}} P^+ + e^-$$
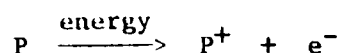
This will be the dominant process in producing charged soot particles.

<u>Diffusive Charging</u>:

$$P + M^+ \rightarrow PM^+$$
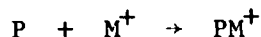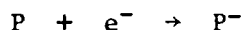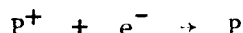
This process will be important when chemical additives of low ionization potential are used to influence soot formation.

<u>Electron Attachment</u>:

$$P + e^- \rightarrow P^-$$

<u>Charged Particle-Electron or Ion Recombination</u>:

$$P^+ + e^- \rightarrow P$$

$$P^+ + M^- \rightarrow PM$$

Because negative ion concentrations are usually smaller than electron concentrations and the rate coefficients are smaller, only electron recombination is considered of importance. This situation changes when electron attachment is important, i.e., low temperatures and large particles.

<u>Proton or Hydride Ion Removal from Charged Particles</u>:

$$PH^+ \rightarrow P + H^+$$

$$PH^- \rightarrow P + H^-$$
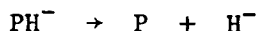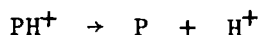
For energetic reasons this process would be considered only in a reaction in which the proton or hydride ion becomes attached to a molecular species. The process then becomes equivalent to an ion-molecule reaction:

$$PH^+ + M \rightarrow P + MH^+$$
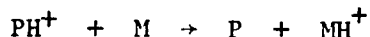
for which the rate coefficient will be very large if the overall process is exothermic. To estimate this rate coefficient the energetics of the proton or hydride ion removal from charged particles was calculated.

<u>Coagulation</u>:

The rate of coagulation or agglomeration for particles of equal diameter, d, which are small compared to their mean free path, is calculated by the equation:

$$\frac{dN_P}{dt} = k_c N_P^2$$

where:

$$k_c = 0.866 \, d^{1/2} \left(\frac{kT}{\rho_p} \right)^{1/2} G \cdot \alpha \cdot S$$

in which ρ_p is the density of the particle, G is a complicated function which takes into account particle dispersion and electrostatic forces, α is the collision integral for a self-preserv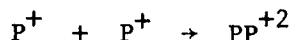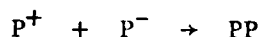ing size distribution, and S is a sticking coefficient. The factor G has been calculated for soot particles of varying diameter for the following processes and is presented in Fig. 2.

$$P + P \rightarrow PP$$

$$P^+ + P^- \rightarrow PP$$

$$P^+ + P^+ \rightarrow PP^{+2}$$

$$P^- + P^- \rightarrow PP^{-2}$$

The rates of the last two reactions are equivalent.

The above quantitative considerations will be very useful in evaluating the relative importance of various processes in sooting flames and should be especially useful in explaining the role played by chemical additives in affecting soot formation in flames. To demonstrate this usefulness we chose the atmospheric pressure ethylene-air flame studied by Haynes, Jander, and Wagner[21] to which they added alkali metals and alkaline earths. They measured the particle number density with and without various additive (seed) concentrations as a function of distance above the burner. The detailed conditions for this flame are given in Table I. We will treat only one point, 2.2 cm above the burner. At this point we calculate the characteristic times for the various processes as indicated on Fig. 3. The significance of being able to make such calculations is that it permits one to choose which processes to consider in a detailed model. It also gives a quantitative understanding of the system. The characteristic times vary over five orders of magnitude; those falling far shorter than the characteristic flow time must be considered infinitely fast and those far longer than the characteristic flow time to be infinitely slow. This flame demonstrates that potassium will give different results depending upon whether or not chemi-ions are present; larger concentrations of potassium ions are obtained from chemi-ion transfer than by thermal ionization. When no
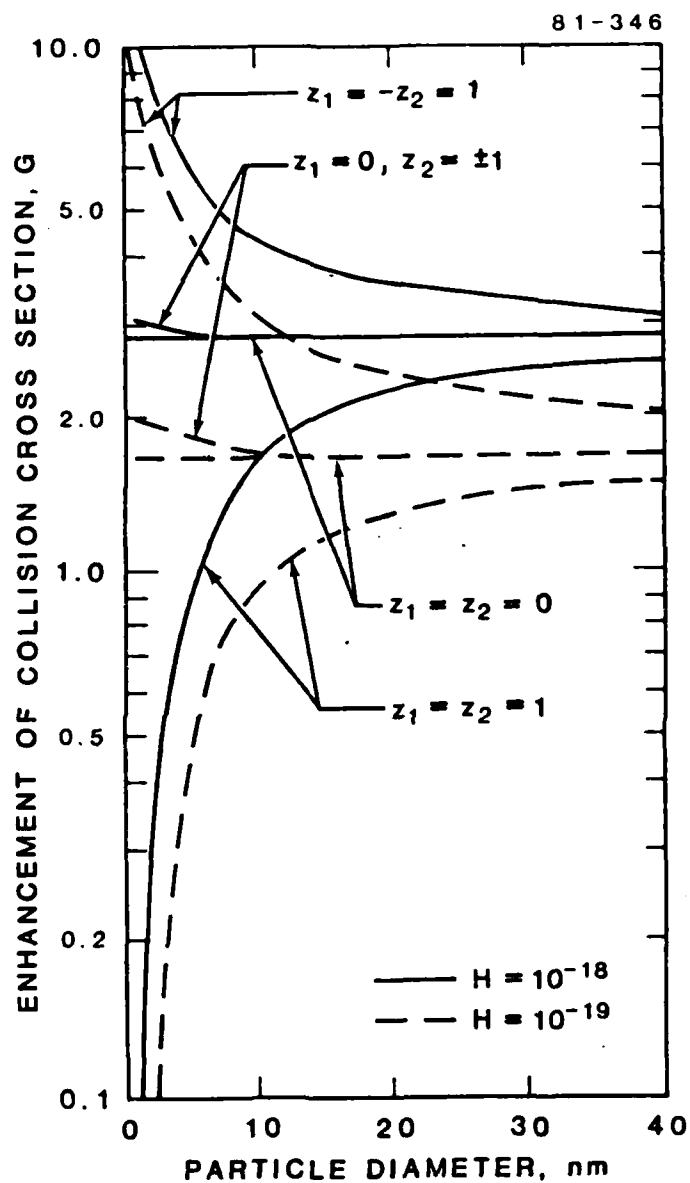
81-346

FIGURE 2 THE EFFECT OF VAN DER WAALS AND ELECTROSTATIC FORCES
ON THE COLLISION CROSS SECTION FOR TWO EQUAL
DIAMETER SOOT PARTICLES

Z = charge on the particle.
H = Hammacker constant.

potassium is present, the ions produced by chemi-ionization, e.g., $C_3H_3^+$, will disappear by dissociative recombination with electrons. When potassium is present, charge transfer will occur extremely rapidly producing K^+, which then disappears very slowly by three-body recombination. An additional effect which must be considered is the removal of $C_3H_3^+$ by the transfer of charge to K thus interfering with the initial ion-molecule steps in soot nucleation, e.g.:

$$C_3H_3^+ + C_2H_2 \rightarrow C_5H_3^+ + H_2$$
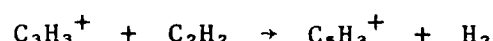
Calculation of the half-life for this process, assuming 0.1% acetylene, gives a value of about 10^{-7} s. Thus, at the concentration of potassium present in the Haynes et al. flame, the nucleation step is not affected. Further examination of Fig. 3 shows that diffusive charging of the soot particles, P, by potassium ions is much faster for larger particles than for smaller particles. The effect of particle charge on the coagulation rate is greatest for small particles.

From a consideration of the results presented here, it is clear why the addition of alkali metals to this flame affects the particle size and particle number density. It is also clear that we are in a position to develop detailed quantitative models—in which the important processes are considered simultaneously—of the effect of chemical additives on soot formation.

TABLE I

PROPERTIES OF ETHYLENE-AIR FLAME OF HAYNES, JANDER, AND WAGNER[21]

Distance above burner 2.2 cm

| Property	Value
Equivalence ratio	2.28
Temperature	1740 K
Time from flame front	25 ms
Unseeded particle diameter	37 nm
Unseeded particle number density	3.2×10^9 cm^{-3}
Potassium seed concentration	3.8×10^{12} cm^{-3}
Seeded particle diameter	13 nm
Seeded particle number density	2.9×10^{10} cm^{-3}
Equilibrium potassium ion concentration	4.3×10^8 cm^{-3}
Potassium ion concentration via chemi-ionization (estimate)	$\sim 5 \times 10^9$ cm^{-3}
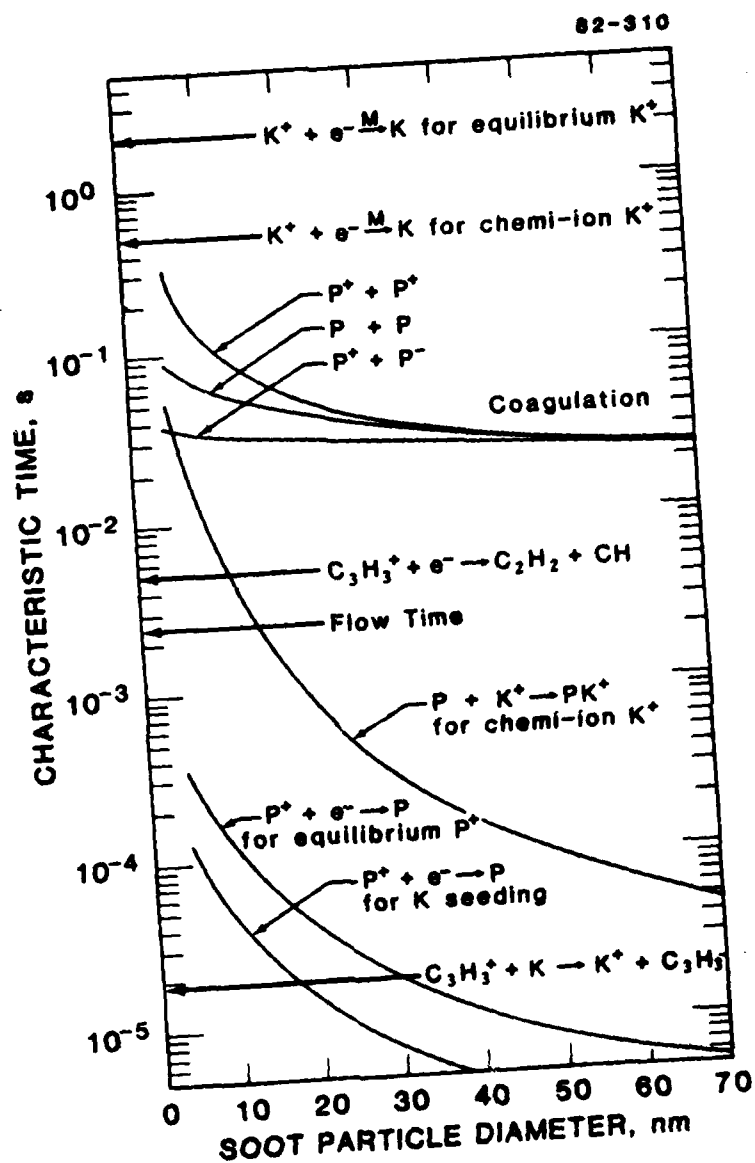
FIGURE 3 CHARACTERISTIC TIMES FOR SOME REACTIONS IN AN ETHYLENE-AIR FLAME AT 1 ATM

Measurements from Haynes, Jander, and Wagner.[21] Equivalence ratio, 2.28. At 2.2 cm above burner. 25 ms.

C. SOOTING FLAME STRUCTURE STUDIES

1. Langmuir Probe Measurements

Olson and Calcote[7] previously reviewed several recent attempts to determine absolute positive ion concentrations in low pressure sooting premixed C_2H_2/O_2 flames at $\phi \approx 3$. Both electrostatic probe and molecular beam sampling were used and the reported absolute ion concentrations varied over more than 2 orders of magnitude. As pointed out, much of this discrepancy may be related to which mass distribution of ions was either measured or thought to be measured.

In order to resolve the question of the absolute ion concentrations in these flames and to improve our understanding of the ion contribution to soot formation, we have employed the electrostatic probe technique to determine absolute ion concentration profiles in laminar premixed C_2H_2/O_2 flames at 2.67 kPa with equivalence ratios varying from $\phi = 1.5$ to $\phi = 4.0$ (from near stoichiometric to heavily sooting flames). An 8.6 cm diam water-cooled stainless steel burner was used with unburned gas velocities of 50 cm s^{-1}.

The use of a Langmuir probe in a flame containing large molecular ions and small charged particles turned out to be new. Thus, a theoretical and experimental comparison of probe theories was made and it was determined that for nonsooting and near-sooting flames the theories of Calcote[22] and Clements and Smy[23] could be used, and for sooting flames, the thick sheath convective theory of Clements and Smy was applicable. (A publication for Combustion and Flame describing this work is in preparation.) Ion mobilities for large ions at high temperatures are required input for these theories; such data were not available. A semi-empirical equation was thus developed,[9] from the theories of ion mobility and the limited available data, to give ion mobilities of large ions as a function of temperature. The next limitation on these measurements was the need to know the molecular weights of the ions in the systems; these are not generally available, so they were estimated from data on similar systems. Figure 4 shows a schematic flow diagram of the procedure used to analyze the probe data.

Two water-cooled copper jacketed probe configurations were used: a "fixed" probe and a "pulsed" probe in which the probe wire could be withdrawn into the cooled support jacket. This permitted rapid probe current measurements (1-2 s) in sooting environments to minimize complications due to soot coating the probe. The probe wires were 0.025 cm diam Pt-10% Rh insulated from the cooling jackets with fine quartz capillaries and were biased relative to the grounded burner with variable dc power supplies. Good agreement was obtained between the two probes; a standard deviation of about 25% was typical.

83-204

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┌─────────────────────────────┐
│     TEMPERATURE PROFILES     │
└─────────────────────────────┘
        │        (THERMO.)
        │           │
        │           ▼
        │      ┌──────────────┐      ┌────────────────────┐
        │      │ COMPOSITION  │      │  CHARGED PARTICLE  │
        │      └──────────────┘      │    MASS PROFILE    │
        │                            └────────────────────┘
        │   (BLANC'S LAW)        (DATA, LANGEVIN)
        ▼      ▼                        ▼
┌──────────────┐              ┌────────────────────────┐
│ LOCAL FLOW   │              │  ION MEAN FREE PATH    │
│  VELOCITY    │              │     ION MOBILITY       │
└──────────────┘              └────────────────────────┘
                                  (CHOICE OF THEORY)
┌──────────────┐          ┌──────────────────┐
│    PROBE     │          │    TOTAL ION     │
│   CURRENTS   │          │  CONCENTRATION   │
└──────────────┘          │     PROFILES     │
                          └──────────────────┘
┌──────────────┐
│  MASS SPEC.  │
│   CURRENTS   │
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                  ┌──────────────────┐
                  │   MASS SPEC.     │
                  │  CALIBRATION     │
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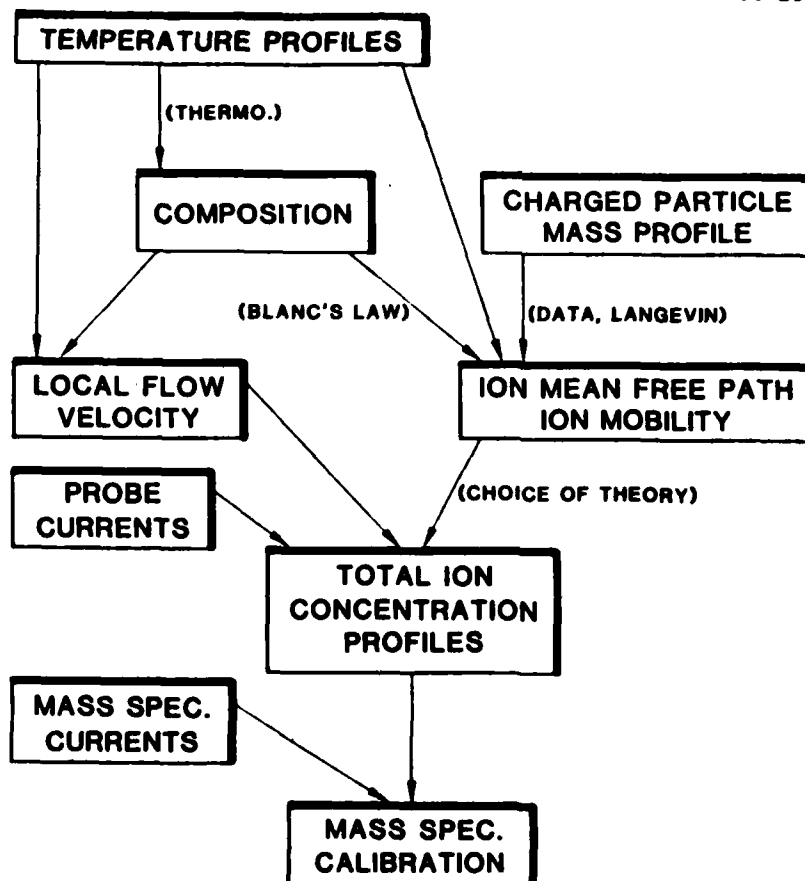
FIGURE 4   SCHEMATIC DIAGRAM OF LANGMUIR PROBE ANALYSIS AND
MASS SPECTROMETER CALIBRATION

Visible sooting became apparent in the C_2H_2/O_2 flames under study over the range of $\phi \geq 2.4$ to $\phi = 2.5$. The major ion in the leaner flames has been shown to have mass 39 ($C_3H_3^+$). Homann[24] shows that for a $\phi = 2.5$ flame the mass of the major species rapidly increases with distance beyond 1 cm above the burner. The appropriate probe theory was selected based on the use of Homann's mass distribution in flames of $\phi \geq 2.5$ (sooting flames) and mass 39 in leaner flames. For the high voltage "pulsed" probe currents the Clements and Smy (CS) thick sheath convective model[23] was used in the sooting $\phi > 2.5$ flames. The ion concentrations for the nonsooting flames were extracted from "fixed" probe ion currents at the plasma potential using Calcote's theory.[25] The resultant absolute ion concentration profiles are illustrated in Fig. 5. The dashed profiles are based on "fixed" probe--Calcote theory; the solid lines are based on "pulsed" probe--CS thick sheath theory. Note for $\phi = 2.5$, Calcote's theory was used in the low mass region and the CS theory was used in the high mass region (1.8 cm and higher); the agreement is excellent.

The observed trends in both the current profiles and in the absolute ion concentration profiles are similar--the maximum ion concentration shifts away from the burner as ϕ is increased and a drastic decrease in the maximum value (current or ion concentration) is observed from $\phi = 1.5$ to $\phi = 3.0$, followed by a significant increase in ion concentration as ϕ is increased from 3.0 to 4.0. At close to the soot threshold, a second peak appears in the ion profiles. This second peak contains some of the same ions, e.g., $C_{13}H_9^+$ (see subsequent discussion), as the first peak which is ascribed to chemi-ionization. The second peak reaches a minimum, at $\phi = 2.9$, well on the fuel-rich side of the soot threshold, and then rises again with increase in equivalence ratio, Fig. 6. This result refutes the arguments against an ionic mechanism based on reported observations that the total ion concentration increases at the soot threshold.*

In a sooting, $\phi = 3.0$, flame the concentrations measured are in reasonable agreement with measurements by others using molecular beam sampling techniques.

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* Some of this work has been published in Ref. 9 or accepted for presentation at the Twentieth Combustion Symposium.
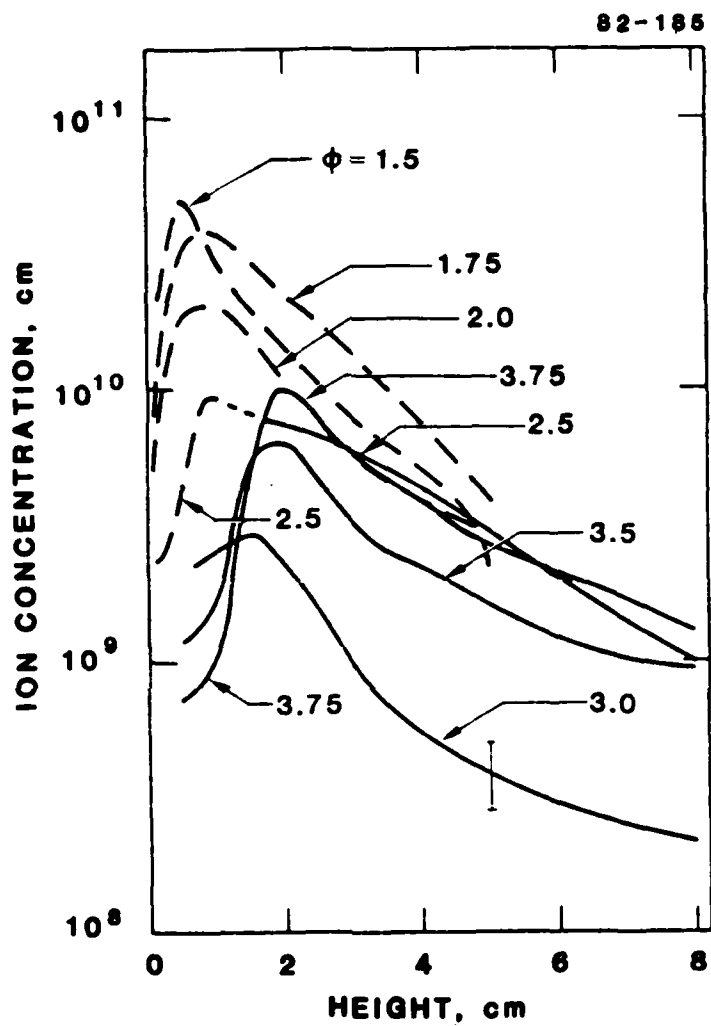
82-185

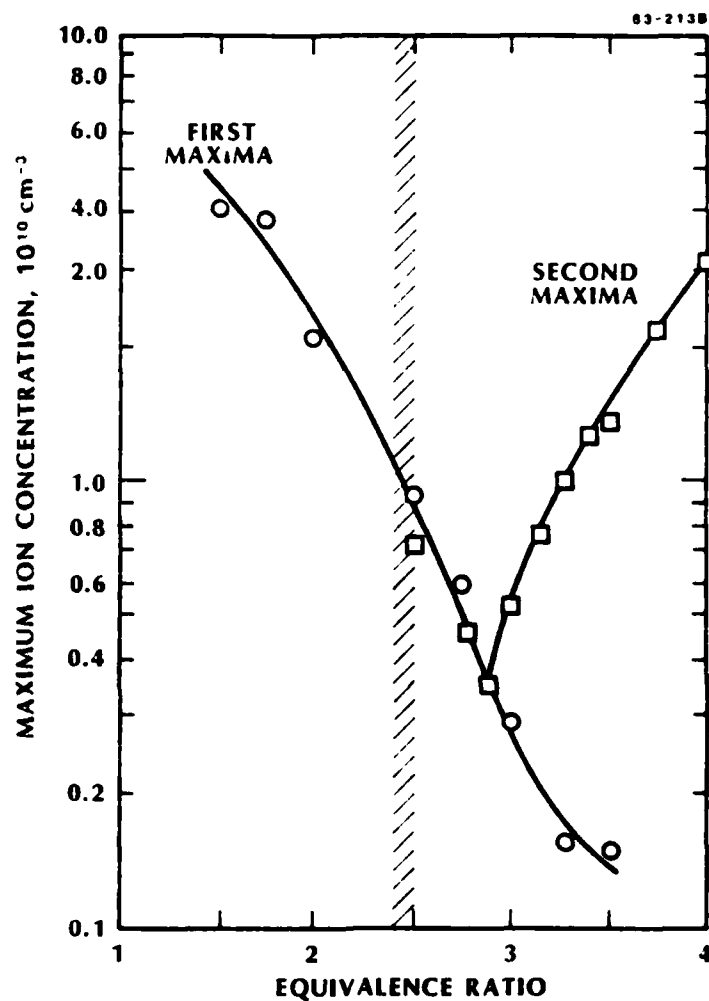FIGURE 5 TOTAL POSITIVE ION CONCENTRATION PROFILES

FIGURE 6   MAXIMUM TOTAL ION CONCENTRATIONS IN PREMIXED ACETYLENE-
OXYGEN FLAMES

The soot threshold was at $\phi = 2.45-2.5$.

2. Mass Spectrometer Calibration

To determine the absolute sensitivity of our flame ion molecular beam sampling quadrupole mass spectrometer over a wide mass range, total ion profiles from Langmuir probe measurements were compared with mass spectrometer individual ion profiles in the 2.67 kPa acetylene-oxygen flames. This effort has not been completed, but over the mass range from 39 to about 200 amu (in nonsooting and moderately sooting flames) a constant sensitivity, i.e., no mass discrimination, has been found. This work needs to be extended to include higher masses, but over part of the mass range the mass spectrometer data can be converted from relative to absolute concentrations. Several schemes have been devised to experimentally extend the calibration to a wider mass range but they were too complicated to consider within the constraints of the present program.

3. Mass Spectrometer Results

We have continued to analyze ion and charged particle concentrations using the ion mass spectrometer on flames with equivalence ratios from 1.5 to 3.0 (the soot threshold is at $\phi = 2.4$). These results, in agreement with the Langmuir probe results, show that these flames exhibit more than one maximum in the concentration vs. distance (or equivalently time) profiles. For example, Figs. 7 and 8 show profiles of $C_{13}H_9^+$, mass 165, and $C_{19}H_{11}^+$, mass 239, respectively, with clearly defined dual maxima which change in relative magnitude with increasing equivalence ratio.* We do not understand the nature of the phenomena causing this second maximum; it is also observed for neutral species.

D. EFFECT OF MOLECULAR STRUCTURE ON SOOT FORMATION

A paper submitted previously to Combustion and Flame was revised and appeared[26] in the journal.

E. EFFECT OF TEMPERATURE ON SOOT FORMATION

A short communication published[27] in Combustion Science and Technology demonstrated, using literature soot thresholds and adiabatic flame temperatures calculated at the soot threshold equivalence ratio of each fuel, that generally

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* Some of this work has been published in Ref. 9 or accepted for presentation at the Twentieth Combustion Symposium.
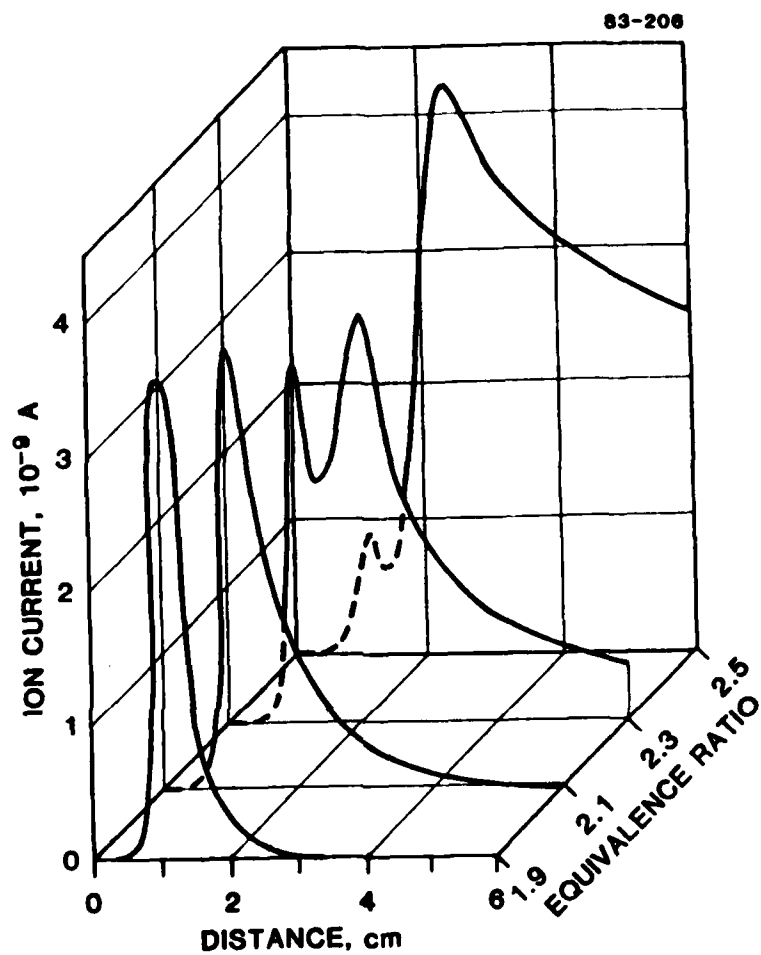
83-206

FIGURE 7 $C_{13}H_9^+$ PROFILES IN ACETYLENE-OXYGEN FLAMES

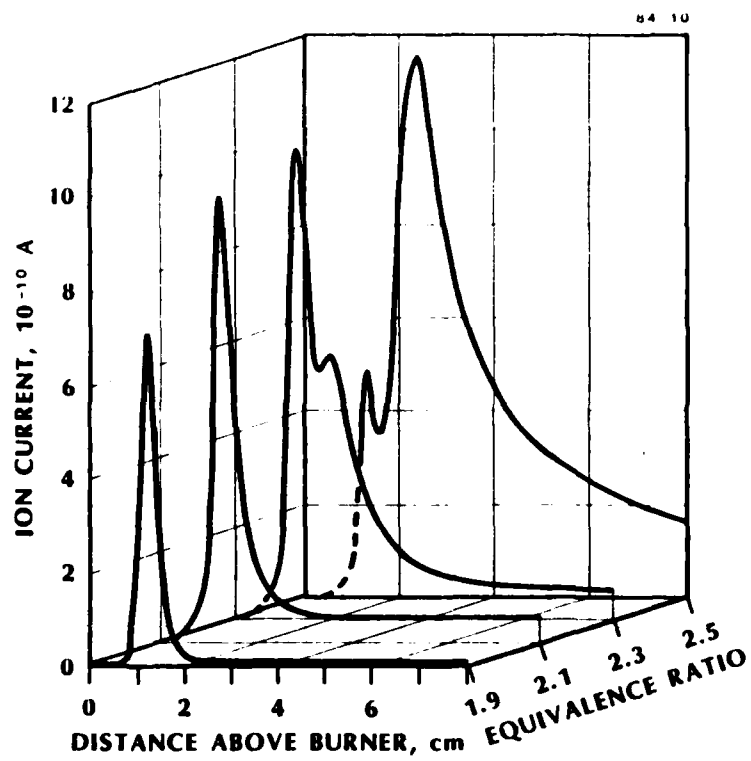Pressure = 2.1 kPa; soot threshold at $\phi \approx 2.4$.

FIGURE 8 $C_{19}H_{11}^{+}$ PROFILES IN ACETYLENE-OXYGEN FLAMES

Experimental conditions as in Fig. 7.

the temperature at the soot threshold increases for various fuels with increasing sooting tendencies. This effect is in the opposite direction of the shift in soot threshold which is observed for a single fuel. For any single fuel, the sooting tendency decreases with increasing flame temperature.

An experimental study was subsequently performed in which the variation in soot thresholds with flame temperature (varied from 1700 to 2400 K by varying $O_2/(N_2 + O_2)$ from about 0.1 to 0.3) was measured for ethylene, propane, decalin, benzene, toluene, and n-heptane. In all cases the soot threshold equivalence ratio increased with increasing temperature.

The effect of temperature on soot yield (soot concentration) was also measured for similar decalin and toluene flames using a multiwavelength laser extinction technique. For a fixed $O_2/(N_2 + O_2)$, the soot yield increased exponentially with increasing equivalence ratio, ϕ. Reducing $O_2/(N_2 + O_2)$ (i.e., decreasing the flame temperature) increased the quantity of soot produced at any given ϕ. Temperatures were both calculated with an adiabatic equilibrium computer program and measured using two-wavelength pyrometry on the soot blackbody emission. The log of the soot yield decreased linearly with increasing temperature indicating the importance of flame temperature (see Fig. 9). At any temperature, the soot yield from toluene exceeds that for decalin (e.g., 30% greater at 1700 K).

Thus changes in flame temperature have been found to shift soot thresholds and soot yields in similar directions. Decreasing flame temperatures slightly increase the threshold soot index (with a small temperature dependence) but greatly increase soot yields (with a large temperature dependence).

Further analysis of these data is necessary before publication.

F. MEASUREMENT OF RATE OF ION FORMATION

Preliminary experiments to measure rates of ion formation by a saturation current technique on premixed propane and ethylene flames at 1 atm were carried out. At the soot threshold, saturation currents increase with decreasing ϕ and increasing $O_2/(N_2 + O_2)$. These measurements are incomplete.
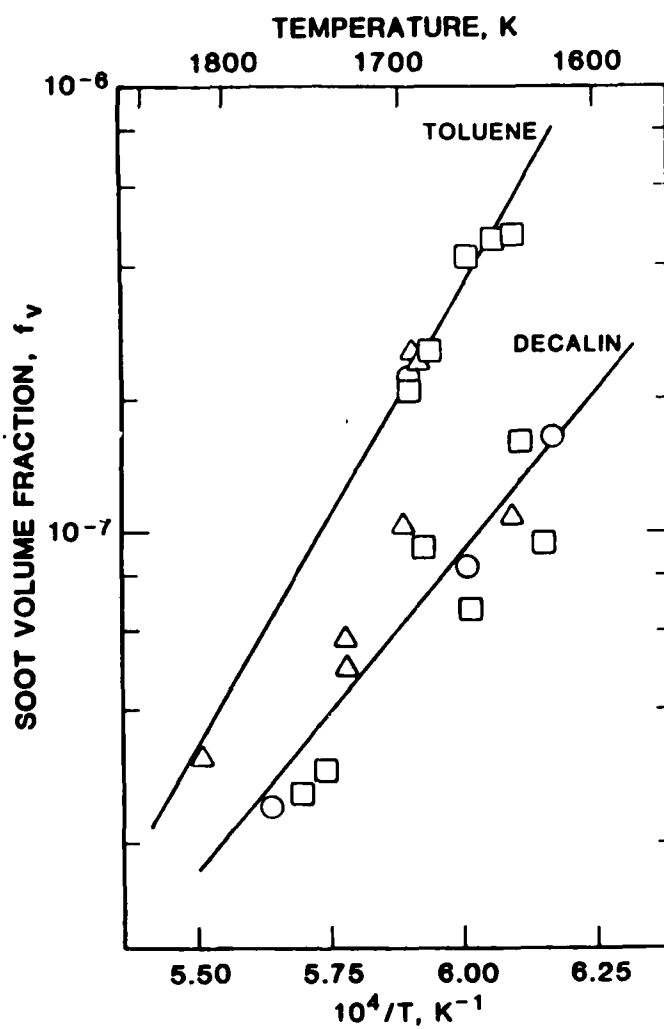
83-205

FIGURE 9   SOOT CONCENTRATIONS IN PREMIXED FLAMES

$\bigcirc$ = air; $\square$ = air + N_2; $\triangle$ = air + O_2

TP-443

III. PUBLICATIONS

The following have been published:

1. "Importance of Temperature on Soot Formation in Premixed Flames,"
    Calcote, H.F. and Olson, D.B., AeroChem TP-416, Combustion Science
    and Technology 28, 315-317 (1982).

2. "Effect of Molecular Structure on Incipient Soot Formation," Calcote, H.F.
    and Manos, D.M., AeroChem TP-406a, Combustion and Flame 49, 289-304 (1983).

3. "Ionic Mechanisms of Soot Formation," AeroChem TP-415, in Soot in
    Combustion Systems and Its Toxic Properties, J. Lahaye and G. Prado,
    Eds. (Plenum Press, New York, 1983) pp. 197-215.

The following manuscripts are in preparation:

4. "The Role of Ions and Charged Particles in Soot Formation," Calcote,
    H.F., an invited review for Progress in Energy and Combustion Science.

5. "Temperature Effects on Soot Formation in Premixed Flames," Olson,
    D.B., for Combustion Science and Technology.

6. "Langmuir Probe Measurements in Sooting Flames," Keil, D.G., Gill,
    R.J., Olson, D.B., and Calcote, H.F., for Combustion and Flame.

IV. PERSONNEL

In addition to the authors, Drs. R.J. Gill and D.G. Keil contributed signi-
ficantly to progress on this project. Several other AeroChem personnel have
also contributed their talents to various tasks, especially to the experimen-
tal measurements, which are tedious and sometimes dirty because the fine parti-
cles of soot tend to collect everywhere and spread to clean hands, clothes,
and papers. The participation of the following personnel is thus gratefully
acknowledged:

> J. Allen, PhD, Physicist
> J.J. Houghton, Research Associate
> J.C. Pickens, Research Technician
> R. Taweel, Technician
> H. Rothschild, Librarian and Technical Editor

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V. TECHNICAL INTERACTIONS

Technical interactions with other members of the scientific community have taken several forms, the foremost of which has been presentations of our work in progress at scientific meetings and workshops. AeroChem organized and hosted an informal workshop on soot formation on 6 May 1981 with 17 people in attendance. This workshop formed an excellent basis for exchange of research information which was not yet published or, in some cases, even interpreted. Comments by the attendees following the workshop were all positive. Other technical interactions include proposal and manuscript reviews which seem to have increased in number in subjects related to ionic effects on soot formation. This activity is due, in part, to our efforts on this contract, championing the ionic theory of soot formation. Personal contacts with other technical people in this field have been maintained by attending meetings, and by correspondence and phone calls.

Presentations

1. "Kinetics of Ion-Molecule Reactions," Calcote, H.F., "Workshop on Plasma Chemistry in Technology," Ashkelon, Israel, 30 March-1 April 1981.

2. "Mechanism of Soot Formation in Flames," Calcote, H.F., Seminar at University of Beer-Shiva, Israel, 3 April 1981.

3. "Ionic Mechanisms in Soot Formation," Calcote, H.F., NATO Workshop on Soot in Combustion Systems," Le Bischenberg, France, 31 August- 3 September 1981. TA-242.

4. "Ionic Mechanisms of Soot Formation in Flames," Calcote, H.F. and Olson, D.B., AFOSR Airbreathing Combustion Dynamics Meeting, Clearwater, FL, 16-20 November 1981. TA-246.

5. "Ion and Charged Particle Contribution to Soot Formation in Flames," Calcote, H.F., Invited presentation at First Annual Conference, American Association for Aerosol Research, Santa Monica, CA, 17-19 February 1982. TA-250.

6. "Chemi-Ionization as the Soot Precursor Step in Soot Formation," Calcote, H.F., Invited presentation at Fall Technical Meeting, American Physical Society, Philadelphia, PA, 3-5 November 1982. TA-255.

7. "Absolute Ion Concentrations in Premixed Acetylene-Oxygen Flames," Keil, D.G., Gill, R.J., Olson, D.B., and Calcote, H.F., Fall Technical Meeting, Eastern Section, The Combustion Institute, Atlantic City, NJ, 14-16 December 1982. TA-259.

8. "Ionic Mechanism of Soot Formation in Flames," Calcote, H.F. and Olson, D.B., AFOSR Airbreathing Combustion Dynamics Meeting, Clearwater, FL, 1-4 November 1982. TA-261.

9. "Ion Concentrations in Premixed Acetylene-Oxygen Flames," Keil, D.G., Gill, R.J., and Olson, D.B., Chemistry of Combustion Processes Symposium, 185th National Meeting, American Chemical Society, Seattle, WA, 20-25 March 1983. TA-264.

10. "Ionic Mechanisms of Soot Formation in Flames," Calcote, H.F. and Olson, D.B., AFOSR Contractors Meeting on Airbreathing Combustion Dynamics Research, Scottsdale, AZ, 19-23 September 1983. TA-272.

VI. INVENTIONS AND PATENT DISCLOSURES

There are no inventions or patent disclosures to report.

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9. Keil, D.G., Gill, R.J., Olson, D.B., and Calcote, H.F., "Ion Concentrations in Premixed Acetylen-Oxygen Flames Near the Soot Threshold," in The Chemistry of Combustion Processes, T.M. Sloane, Ed., ACS Symposium Series 249 (American Chemical Society, Washington, DC, 1984) p. 33.

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23. Clements, R.M. and Smy, P.R., "Electrostatic-Probe Studies in a Flame Plasma," J. Appl. Phys. 40, 4553 (1969).

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